DIRECT DETERMINATION AND QUANTIFICATION OF SULFUR FORMS IN COALS
FROM THE ARGONNE PREMIUM SAMPLE BANK

Martin L. Gorbaty, Graham N. George, Simon R. Kelemen and Michael Sansone
Exxon Research and Engineering Company
Annandale, NJ 08801

Keywords:  Organic Sulfur, XANES, XPS, Rank

Sulfur K Edge X-ray Absorption Near Edge Structure Spectroscopy (XANES) and
X-ray Photoelectron Spectroscopy (XPS) have been developed for the direct
determination and quantification of the forms of organically bound sulfur in
nonvolatile petroleum and coal samples.  XANES and XPS spectra were taken of a
number of model compounds, mixtures of model compounds, heavy petroleum and
coal samples.  A third derivative analysis of the XANES spectra and curve
resolution of the XPS spectra allowed approximate quantification of the
sulfidic and thiophenic components of the model mixtures and heavy hydrocarbon
resources.  Both techniques were used to characterize organically bound sulfur
forms in coals from the Argonne Premium Coal Sample Bank and both show a
monotonic increase of thiophenic sulfur with increasing rank.

Introduction

X-ray Absorption Near Edge Structure (XANES) Spectroscopy and X-ray
Photoelectron Spectroscopy (XPS) are two techniques which have been applied
recently for the direct speciation and approximate quantification of
organically bound forms of sulfide and thiophenic sulfur in nonvolatile liquid
and solid carbonaceous materials (1-5).  Both techniques have been used to
characterize the levels of sulfide and thiophenic sulfur forms in coals from
the Argonne Premium Coal Sample Program and to develop a correlation of sulfur
forms with rank.

It is known that organic sulfides can be converted to thiophenes on heating.
For example,it has been shown that when benzylsulfide is heated to 290°C,
tetraphenylthiophene, hydrogen sulfide and stilbene are produced (6).
Extending this to organically bound sulfur forms in coals, it would be
expected that the ratio of thiophenic sulfur to sulfide sulfur would increase
with increasing rank, as the coal precursor materials experience more and more
severe geological temperatures and pressures during metamorphism.  Recent data
on a number of coals of different rank, obtained by flash pyrolysis
experiments (7) which measure and correlate $H_2S$ evolution with level of
sulfide sulfur present indicate this trend. However, these experiments leave
open the question as to whether sulfur forms are interconverting during the
pyrolysis.  $H_2S$ evolution may not correlate directly with sulfide sulfur and
coupled with heat and mass transport limitation considerations, particularly
for solids, it is not unreasonable to question whether at least some of the
thiophenic forms observed by pyrolysis techniques are produced during heating.
Therefore, the forms of organically bound sulfur in coals of different rank
obtained from the Argonne Premium coal sample program were determined by
direct measurement using XPS and XANES.

Experimental

The procedures for obtaining XANES and XPS spectra have been discussed
elsewhere (1-4).  The XANES spectra were recorded at the National Synchrotron
Light Source at Brookhaven National Laboratory on line X-10C. To avoid ambient
temperature oxidation, sample preparations were done in a glove bag filled

with nitrogen. Coal samples, which were all <100 mesh as-received, were dusted onto mylar tape and the sample holders transported to the beamline in nitrogen filled bottle. Similarly, preparation of samples for XPS were done in a nitrogen filled dry box, and the samples inserted into a fast entry air lock. Fluorescence XANES spectra were recorded using a Stern-Heald-Lytle detector (8). Pyrite interferences in the XANES spectra were removed by subtracting the third derivative spectrum of iron pyrite from the third derivative spectrum of the coals until the lowest energy pyrite "peak" was removed. Pyrite interferences in the XPS data from Illinois #6 coal were removed by subtraction during the curve resolution analysis by the method described previously (3). The accuracy of both the XANES and XPS methods for determining organically bound sulfide and thiophenic sulfur forms is estimated to be ± 10%.

Results

XANES spectra and their third derivative traces for the 8 Argonne Premium samples are shown in Figure 1. The feature at about 2468.5 eV is associated with pyritic sulfur, that at 2469.8 eV with sulfide sulfur and 2470.4 eV with thiophenic sulfur. After subtracting pyrite interferences, measurement of peak heights from the baselines provided the approximate quantifications of sulfide and thiophenic sulfur forms found in these samples. These data are listed in Table 1 and plotted in Figure 2 against carbon content of the coals. Except for the Illinois #6 data, there is a clear increase in thiophenic sulfur with increasing carbon content of the coals.

XPS data on the same samples are also shown in Table 1 and are plotted in Figure 2. With the exception of Illinois #6 coal, it was possible to curve resolve the organic sulfur 2p spectrum using sulfur species components fixed at 163.3 eV and 164.1 eV for sulfide and thiophenic sulfur respectively. The sulfur signals representative of these single species under the experimental conditions of this and previous studies (4,5) were determined from the instrumental response to pure sulfur model compounds. The signal of a single sulfur species is composed of two peaks representing 2p3-2 and 2p1-2 components having a 2:1 relative intensity and separated in energy by 1.2 eV. Each component is composed of equally mixed Gaussian and Lorentzian line shapes and a full width-half maximum of 1.4 eV. These conditions were used for all curve resolving procedures. The XPS data confirm the trend of increasing thiophenic sulfur content with increasing rank.

Pyritic sulfur was observed only in the Illinois #6 spectrum. The XPS spectra in the unoxidized region of all other Argonne Premium samples were found not to contain contributions from pyritic sulfur. A weak iron 2p signal was detected in the spectra of Upper Freeport, Pittsburgh #8, Lewiston-Stockton and Beulah-Zap. The levels, when normalized to the carbon 1s signal were lower than expected from bulk elemental analyses. This behavior has been noted before with other coals (3,9). In every case, a broad peak was centered well below 711 eV, indicative of iron oxides or sulfate in poor electrical contact with the organic matrix. No evidence was found for a pyritic iron signal in this study, and on this basis the XPS sulfur 2p spectra were judged to be free of interference effects due to pyritic sulfur.

Discussion and Conclusions

Both XPS and XANES data confirm the trend of increasing thiophenic sulfur content with rank for the coals studied. This is the first such evidence obtained by direct measurement. Figure 3 shows both sets of data plotted

against each other, the solid line being the parity situation. It is seen that the surface and bulk measurements are in good agreement and fall within the established limits of accuracy for both methods. The implication of this is that sulfur distributions at the surface and in the bulk are similar.

The outlying point in Figures 2 and 3 arises from the XANES data of Illinois #6 coal. If there are errors in the pyrite subtraction procedure, or if absorptions of the thiophenic species actually present are shifted due to substituent effects, the values reported herein for thiophenic sulfur in this coal would be low. These possibilities are under study at this writing.

## Acknowledgments

## References Cited

1) George, G. N.; Gorbaty, M. L. *J. Amer. Chem. Soc.*, *1989, 111*, 3182.

2) George, G.N.; Gorbaty, M.L.; Kelemen, S.R. In Geochemistry of Sulfur in Fossil Fuels; Orr, W.L., White, C.M., Eds.; ACS Symposium Series; American Chemical Society; Washington DC, In press.

3) Kelemen, S. R.; George, G. N.; and Gorbaty, M. L. *ACS Div. Fuel Chem. Preprints*, 1989, *34*, 729.; *FUEL*, 1990, *69*, in press.

4) Gorbaty, M. L.; George, G. N.; Kelemen, S. R. *ACS Div. Fuel Chem. Preprints*, 1989, *34*, 738; *FUEL*, 1990, *69*, in press.

5) Kelemen, S. R.; George, G. N.; Gorbaty, M. L. *Fuel Process. Technol.* 1990, *24*, 425.

6) Fromm, E. and Achert, O. *Ber.*, 1903, *36*, 545.

7) Calkins, W. H., *Energy Fuels*, 1987, *1*, 59; Torres-Ordonez, R. J.; Calkins, W. H.; Klein, M. T. In Geochemistry of Sulfur in Fossil Fuels; Orr, W.L., White, C.M., Eds.; ACS Symposium Series; American Chemical Society; Washington DC, In press.

8) Stern, E; Heald, S. *Rev. Sci Instrum.*, 1979, *50*, 1579.

9) Perry, D. L.; Grint, A. *Fuel*, 1983, *62*, 1029.

**Table 1**

# THIOPHENIC SULFUR INCREASES WITH RANK
## (ARGONNE PREMIUM COAL SAMPLES)

| COAL | % CARBON (daf Basis) | MOLE % (± 10) BY XANES | BY XPS |
|------|------|------|------|
| BEULAH-ZAP | 74.05 | 46 | 55 |
| WYODAK-ANDERSON | 76.04 | 58 | 63 |
| ILLINOIS #6 | 80.73 | 47 | 89 |
| BLIND CANYON | 81.32 | 75 | 65 |
| PITTSBURGH #8 | 84.95 | 77 | 75 |
| LEWISTON-STOCKTON | 85.7 | 74 | 68 |
| UPPER FREEPORT | 88.08 | 89 | 81 |
| POCAHONTAS | 91.81 | 98 | 100 |

**Figure 1**



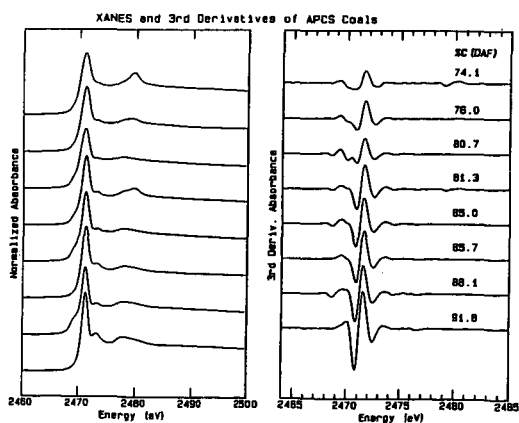XANES and 3rd Derivatives of APCS Coals

## Figure 2

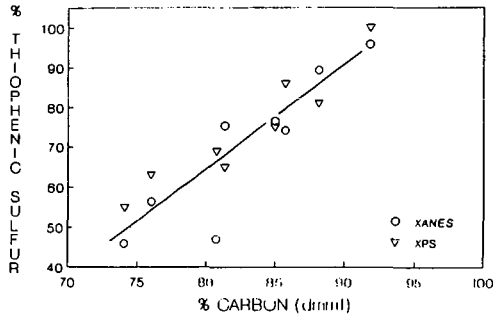### THIOPHENIC SULFUR INCREASES WITH RANK
### ARGONNE PREMIUM COAL SAMPLES



## Figure 3

### XPS/XANES DATA COMPARISON
### (ARGONNE PREMIUM COAL SAMPLES)